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## HIGH SELECTIVITY AND EFFICIENCY IN CLATHRATE CHROMATOGRAPHY

### GENERATION OF ABSORPTION SITES IN THE $\beta$ -Ni(NCS)<sub>2</sub>(4-METHYLPYRIDINE)<sub>4</sub> PHASE BY THE MOBILE PHASE COMPONENTS

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#### SUMMARY

The chromatographic separation of nitroalkanes, dinitrobenzenes and nitronaphthalenes on a column filled with  $\beta$ -Ni(NCS)<sub>2</sub>(4-methylpyridine)<sub>4</sub> clathrates has been studied. These investigations were followed by an examination of the composition and the structure of the sorbents. It has been found that the influence of organic solvents on the sorption is dependent on the nature and the concentration of the solvent, and on the type of compounds to be separated. An attempt is made to explain these effects in terms of the existence of two types of sorption centres and of a competitive sorption mechanism.

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#### INTRODUCTION

Since the clathrates formed by Werner complexes were first applied in chromatography<sup>1</sup>, various isomeric compounds have been separated on these sorbents<sup>2,3</sup>. The chromatographic and physicochemical investigations of the clathrate sorbents have led not only to the understanding of the composition and structure of the sorbents<sup>4,5</sup> but also to the partial understanding of the mechanism of the chromatographic separation processes on the clathrates<sup>6-8</sup>.

We have recently found that it is possible to control the chromatographic processes occurring on the clathrates by changing the composition of the mobile phase. However, it remains to be determined whether such changes influence only the dimensions of the cages and of the channels in the structure of the clathrates, or whether there are any effects on the guest molecules.

We present here the results of attempts to solve this problem by examining the influence of an organic solvent (added to the aqueous mobile phase) on the process of elution from clathrate columns of aliphatic and aromatic compounds. The clathrate sorbents were formed from Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>, where 4-MePy = 4-methylpyridine.

#### EXPERIMENTAL

The solvents and all the reagents were p.a. grade and their physicochemical

constants agreed with those in the literature. The 4-MePy used contained 0.05% of 3-methylpyridine but no 2.5-dimethylpyridine, as detectable by gas chromatography.

Nitroethane, nitropropanes and 1-nitro-*n*-butane were taken as model aliphatic compounds, dinitrobenzenes and 1- and 2-nitronaphthalenes as the aromatic ones.

The basic chromatographic investigations were carried out by means of the chromato-polarographic method and apparatus described by Kemula<sup>9</sup>.

The sorbents were prepared from the clathrate  $[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4] \cdot (4\text{-MePy})_{0.7}$  by the method described earlier<sup>6-8</sup>. The columns (30-35 or 60-70  $\times$  5 mm I.D.) contained 300 or 600 mg of the clathrate. The flow-rate was 8 ml/h. The 5-10- $\mu\text{l}$  samples of the solutions to be investigated, about  $2 \cdot 10^{-3}$ - $4 \cdot 10^{-3}$  *M*, were injected by means of a Hamilton microsyringe. The temperature of the chromatographic column during the experiments was  $25 \pm 1^\circ\text{C}$ .

Standard formulae<sup>10</sup> were employed for calculation of the values of the distribution coefficient, *K*, capacity factor, *k'*, and the separation coefficient,  $\alpha$ . The mean density of the sorbent was assumed to be 1.25 g/cm<sup>3</sup> in these calculations.

The X-ray measurements were carried out using a Rigaku-Denki ( $\text{CuK}_\alpha$ ) diffractometer. The phase analyses of the sorbents were carried out as described previously<sup>11</sup>.

## RESULTS

### Chromatography

Fig. 1 shows a plot of the logarithm of the distribution coefficient *K* of nitropropanes and of 1-nitro-*n*-butane vs. the logarithm of the concentration of methanol

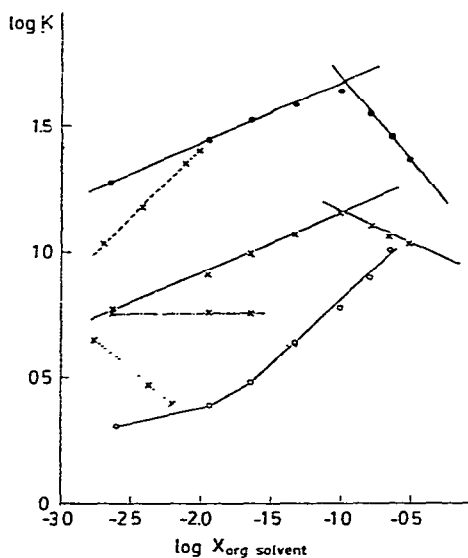


Fig. 1. Plot of  $\log K$  of 1-nitro-*n*-butane (●), 1-nitropropane (×) and 2-nitropropane (○) versus  $\log X_{\text{org solvent}}$ , where  $X_{\text{org solvent}}$  is the mole fraction of an organic solvent in the aqueous mobile phase solution. Organic solvents: methanol (—); ethyl acetate (---); formamide (-·-·-); furfuryl alcohol (···).

in the aqueous mobile phase. The values of concentration are given as mole fractions. The influence of ethyl acetate, furfuryl alcohol and formamide on the distribution coefficient (logarithmic scale), taking 1-nitropropane as an example, is also shown. In each case the mobile phase contained 0.2 mole/l of  $\text{NH}_4\text{SCN}$ , 0.1 mole/l of 4-MePy and various amounts of methanol or of the other investigated solvent.

Table I compares the properties of the clathrate, when contacted with different solvents. The values of the distribution coefficients of nitroethane, nitropropanes and 1-nitro-*n*-butane, determined in the aqueous solutions of the mobile phase, containing 5% (v/v) of different solvents, are shown. The conditions were the same as those corresponding to Fig. 1. The comparatively low solvent concentration [5% (v/v)] was used to avoid too great a variation of the value of the distribution coefficient, caused by the change in solubility.

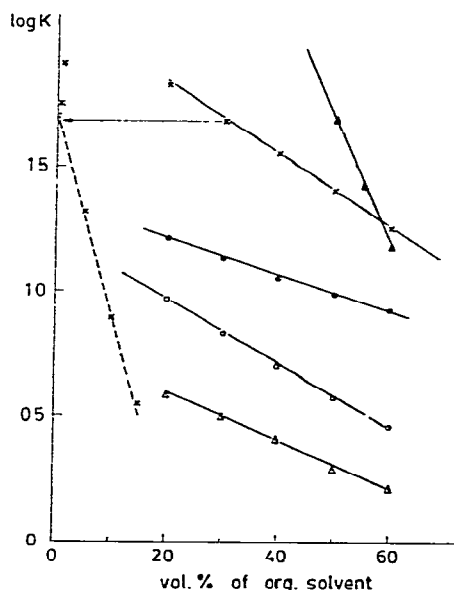


Fig. 2. Plot of  $\log K$  of *o*-dinitrobenzene (○), *m*-dinitrobenzene (●), *p*-dinitrobenzene (×),  $\alpha$ -nitronaphthalene (△) and  $\beta$ -nitronaphthalene (▲) vs. % (v/v) methanol in aqueous mobile phase solution. The values of  $\log K_{p\text{-dinitrobenzene}}$  (×) as a function of % (v/v) ethyl acetate (---) and furfuryl alcohol (···) in 30% (v/v) methanol in water are also shown.

Fig. 2 shows a plot of the logarithm of the distribution coefficient  $K$  of dinitrobenzenes and nitronaphthalenes vs. the concentration of methanol expressed in % (v/v). The influence of ethyl acetate and furfuryl alcohol on the distribution coefficient, taking *p*-dinitrobenzene as an example, is demonstrated. In each case the mobile phase contained 0.1 mole/l of  $\text{NH}_4\text{SCN}$ , 0.2 mole/l of 4-MePy and various concentrations of methanol in water. When other solvents were used, the mobile phases contained 30% of methanol. Methanol was added because of the poor solubility of dinitrobenzenes and nitronaphthalenes in water, which resulted in the very high values of their capacity factor ( $k' > 100$ ) in relation to water.

TABLE I  
DISTRIBUTION COEFFICIENTS,  $K$ , OF NITROALKANES AND CRYSTAL LATTICE PARAMETERS AND MOLAR VOLUMES OF THE CLATHRATES,  $\beta$ -[Ni(NCS)<sub>2</sub>(4-MePy)<sub>4</sub>]<sub>1</sub>·(*n*-4-MePy)<sub>4</sub>·(*m* org. solv.)  
Mobile phase: 0.2 M NH<sub>4</sub>SCN + 0.1 M 4-MePy in water containing 5% (v/v) of the given solvents.

Solvent	$K$	Crystal lattice parameters (Å)				$V_{mol}$ (cm <sup>3</sup> )	
		Nitroethane	2-Nitropropane	1-Nitro- <i>n</i> -butane	$a$ $c$		
Formamide	0.5	1.5	5.7	17.0	17.26	23.63	530.0
Dimethyl sulphoxide	0.8	1.9	6.5	20.0	17.29	23.58	530.7
Ethylene glycol	1.1	2.1	7.6	24.0	17.31	23.55	531.3
Methanol	1.2	3.0	9.9	34.0	17.28	23.54	529.2
Ethanol	1.3	3.7	10.9	38.5			
Acetone	1.7	4.2	12.8	39.5			
Diethylene glycol monomethyl ether	2.7	10.2	23.0	68.0	17.34	23.71	536.7
Ethyl acetate	2.1	15.0	25.0	91.0	17.24	23.20	519.1
Pure water	0.5	1.9	5.7	17.5	17.08	23.26	510.9
2% (v/v) Furfuryl alcohol		1.5	3.0	8.0			

*Investigations of the solid phases*

It has been found that all the column fillings were tetragonal clathrates of the formula  $\beta\text{-}[\text{Ni}(\text{NCS})_2(4\text{-MePy})_4]\cdot\text{G}$ , where G is a mixture of 4-MePy and the organic solvent. The composition of G depends on the concentration of both components in the mobile phase.

Table I gives values of the lattice parameters and the molar volumes of the sorbents.

## DISCUSSION

The investigated clathrates, which comfortably accommodate the molecules of *o*-, *m*- and *p*-disubstituted benzene derivatives, still enable the separation of the isomeric nitroaliphatic compounds, which have very different shapes and volumes.

The results of the present work show that these different selectivities may result from the existence of two types of sorption centres in the crystal lattice of the sorbents. Both centres are generated by the clathrated guest: one by aromatic molecules, such as  $\alpha$ -picoline and furfuryl alcohol, and accounts for the sorption of aromatic molecules; the other by molecules of aliphatic solvents such as methanol and ethyl acetate, and is the potential sorption centre for other aliphatic molecules. Thus, when the methanol concentration is first increased there is a corresponding increase of the value of the distribution coefficient of the nitroalkane; also, the plot of  $\log K$  vs.  $\log$  (mole fraction of methanol) is a straight line, which can be taken as evidence that the new centres are being generated by methanol at the expense of those occupied by 4-MePy, and the capacity towards aliphatic molecules increases. With further increase of the concentration of methanol ( $C > 20\%$ ) the direction of the plot for nitroalkanes reverses. Perhaps in this region the most important processes are the competitive sorption of methanol and the solubilities of nitroalkanes in the mobile phase. The molar volumes of the clathrates can be taken as evidence for this. After the sorbents had been allowed to equilibrate with the mobile phases of different methanol concentrations, the molar volumes were:  $V_{10\%} = 519.9 \text{ cm}^3$ ;  $V_{20\%} = 514.7 \text{ cm}^3$ ;  $V_{30\%} = 515.2 \text{ cm}^3$ ;  $V_{40\%} = 512.8 \text{ cm}^3$ ;  $V_{\text{H}_2\text{O}} = 510.9 \text{ cm}^3$ . The maxima in the molar volumes of the clathrate sorbents and in the  $K$  coefficients for 1-nitro-*n*-alkanes fall approximately in the same range of methanol concentration in the mobile phase.

It should be stressed that only the changes in the composition and structure of the clathrate can be responsible for the increase of the value of  $K$  of nitroalkanes in the initial range of concentration of such solvents as methanol, ethanol, acetone and ethyl acetate. Interactions in liquid solution are not responsible, as was confirmed in reversed-phase systems<sup>12</sup>.

In the case of furfuryl alcohol, only a rapid decrease of the distribution coefficient is observed for all the investigated nitroalkanes. The molecules of furfuryl alcohol behave in a similar manner to those of methylpyridines, generating centres able to sorb aromatic compounds at the cost of the other centres occupied by an aliphatic solvent or water.

The opposite behaviour is found in the case of aromatic compounds. In methanol the values of the distribution coefficients decrease, *i.e.*, the plot of  $\log K$  vs. % (v/v) methanol is linear. This suggests that the predominant effect is the increase

of the solubility of nitroaromatic compounds in the mobile phase, while the corresponding changes in the structure of the sorbent are not large: there is no competitive sorption, as there are different sorption centres for methanol and for nitroaromatic compounds. Other solvents such as ethanol, acetone, diethylene glycol monomethyl ether, ethylene glycol and ethyl acetate give similar results.

One might expect that in the initial region aromatic compounds should facilitate the sorption of nitroaromatic compounds, generating the appropriate sorption centres. We found this effect in our previous study of the influence of various pyridine bases, which accompany 4-MePy (ref. 13). Also in the case of furfuryl alcohol, we found an initial increase in  $K$  for *p*-dinitrobenzene (Fig. 2).

It should be noted here that organic solvents influence not only sorbent capacity but also selectivity. The changes of the retention of 1- and 2-nitropropanes caused by methanol are a good example of this (Fig. 1).

Some support for the above conclusions can be obtained from the results of the phase analysis of the sorbent. From an examination of the structure, two kinds of holes can be distinguished<sup>14</sup>. There is a lack of structural data concerning the occupation of these holes by the differently shaped guest molecules. However, the changes of the lattice parameters (Table I) and the molar volume indicate that the solvents are clathrated: the composition of G changes, but it is difficult to find any simple relation between it and the retention of the investigated compounds.

It appears that the chromatographic investigation of the sorption in clathrates, under appropriate conditions, can be very effective for the detection of minute changes of the structure and the occupation of the holes; this requires low concentrations of a guest, to avoid distortion of the host structure.

#### ACKNOWLEDGEMENT

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